# Ember

## PYROLYSIS TECHNOLOGY FOR HYDROGEN AND CARBON

TNO innovation for life

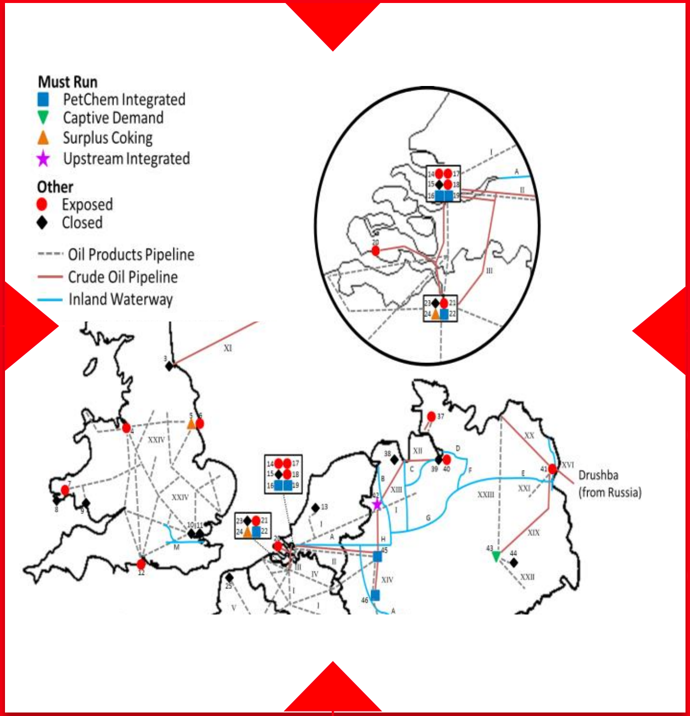
Rajat Bhardwaj, Willem Frens, Marco Linders, Earl Goetheer

# EUROPEAN PETROCHEMICAL (PROCESS) INDUSTRY AT HIGH RISK

innovation for life

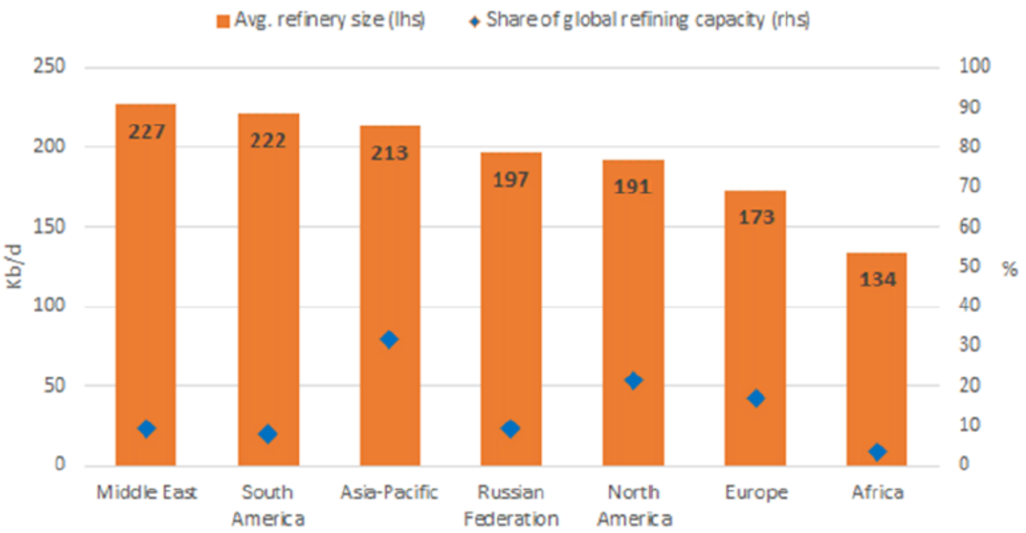
Renewable revolution

Demand contraction




Cost Competition

Climate: Decarbonization




In Rotterdam alone:

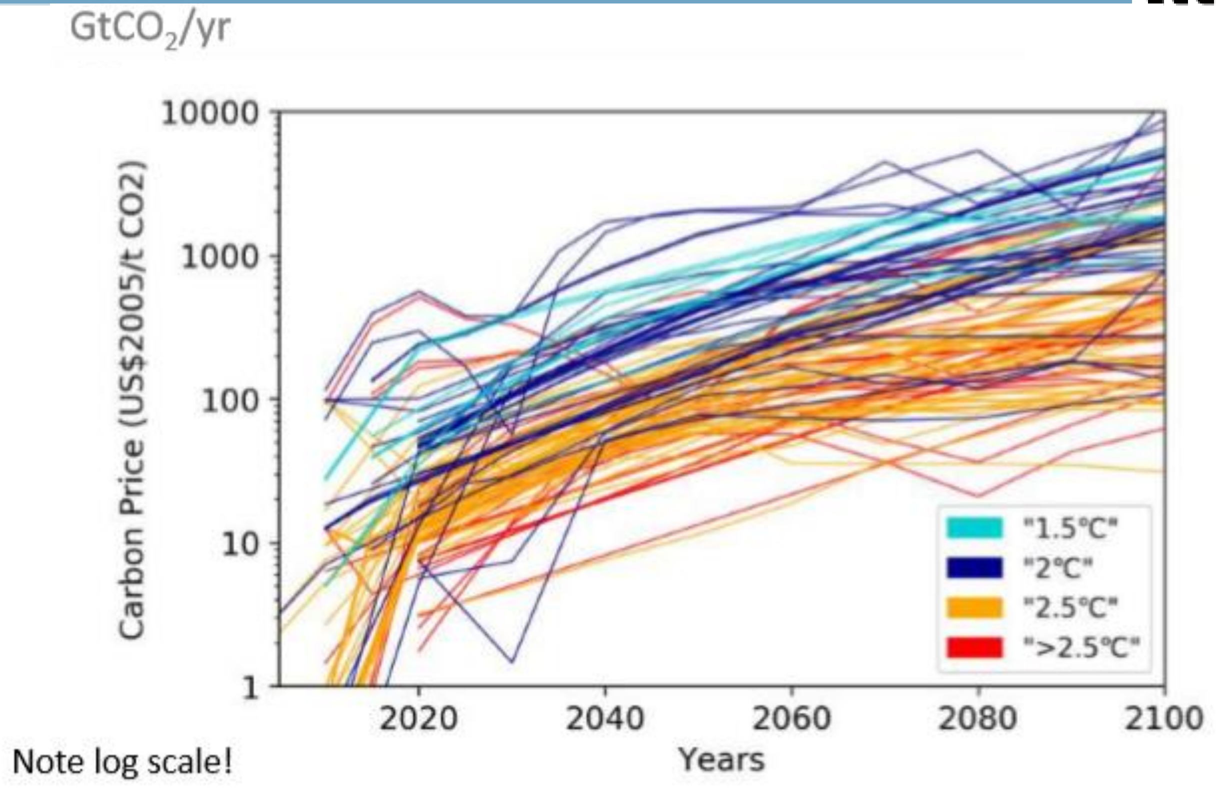
- 250+ Billion Euro capital assets.
- 450 Mtonnes material flow in 2015.
- 6,000 ha of industrial sites.
- >90,000 employed overall in harbor (20,000 @ industrial cluster)

**Only 12 out of 34 refineries in North West Europe must run post 2025.**



Ref. Long-term prospects for northwest european refining, CIEP energy paper.

# URGENCY TOWARDS FIXED CARBON REMOVAL

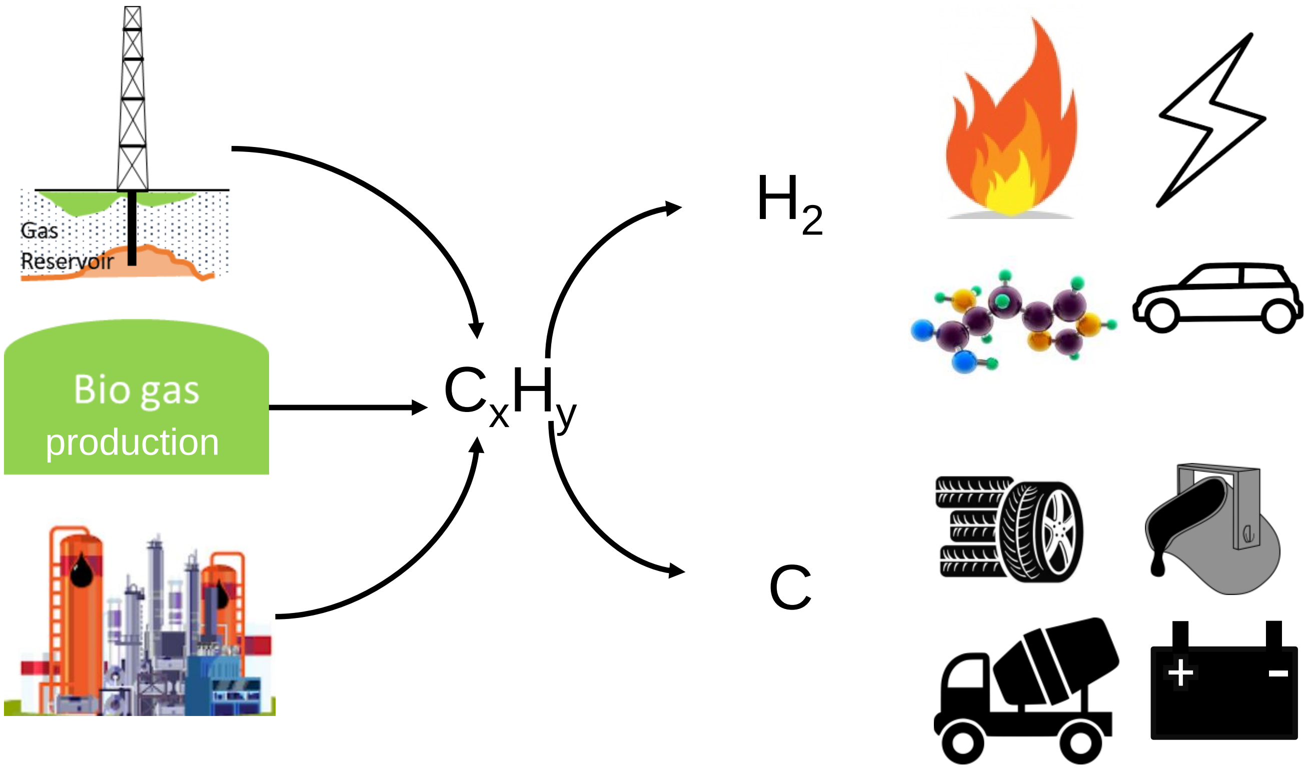



- Bitten more than we can chew - can't reduce faster than 2 GtCO2/yr per year.



Myles Allen et al.

# WHY DO LARGE SCALE PYROLYSIS?




**9 – 11**
tonnes $CO_2$/ton $H_2$

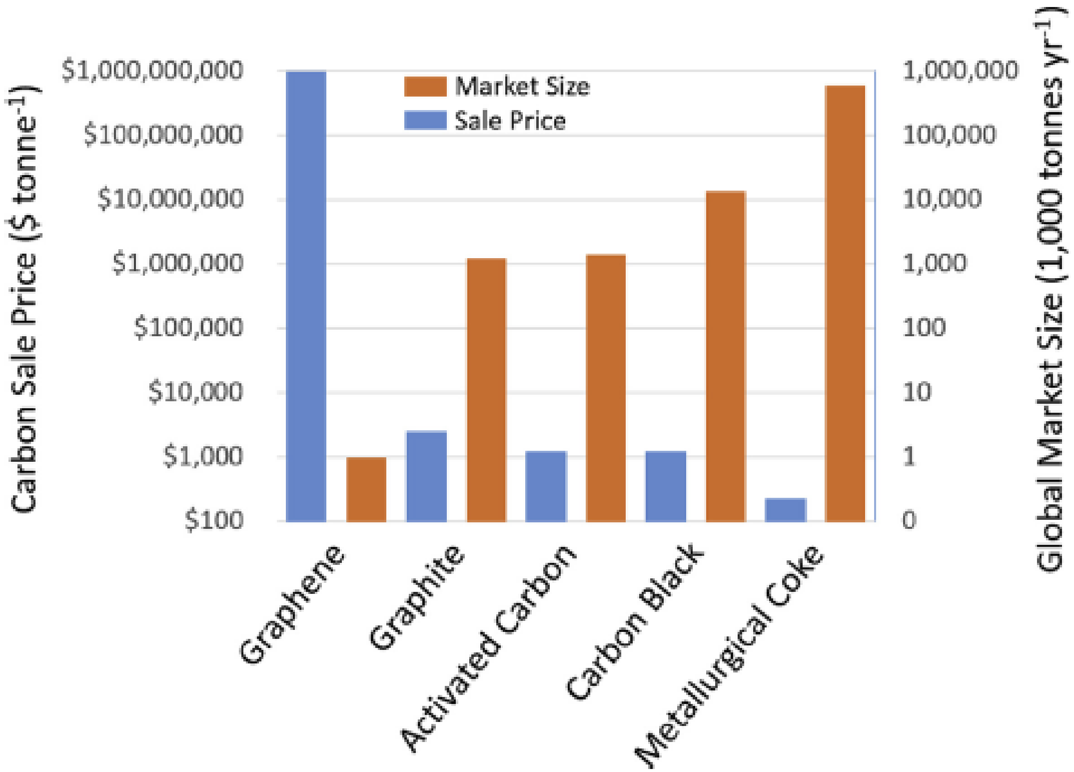
**2.5 – 4.5**
tonnes $CO_2$/ton C

**ABUNDANT RAW MATERIALS**

**$H_2$ & C ARE BASE PRODUCTS**

**>90% $CO_2$ REDUCTION**
**(0 – 2.5 ton $CO_2$/4 ton product)**

# CARBON MARKET FOR DIFFERENT PRODUCTS

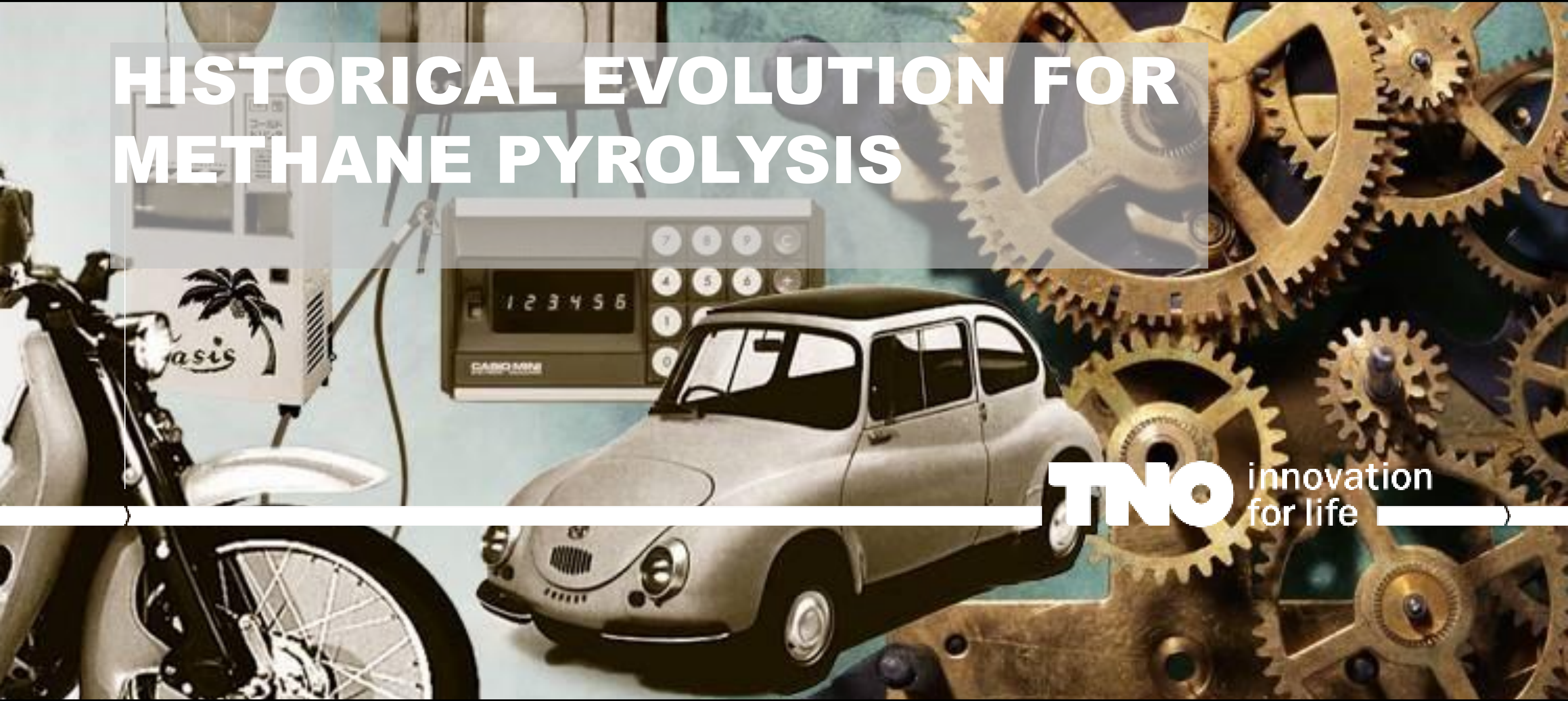



Tuneable carbon technology development can accommodate variety of products.

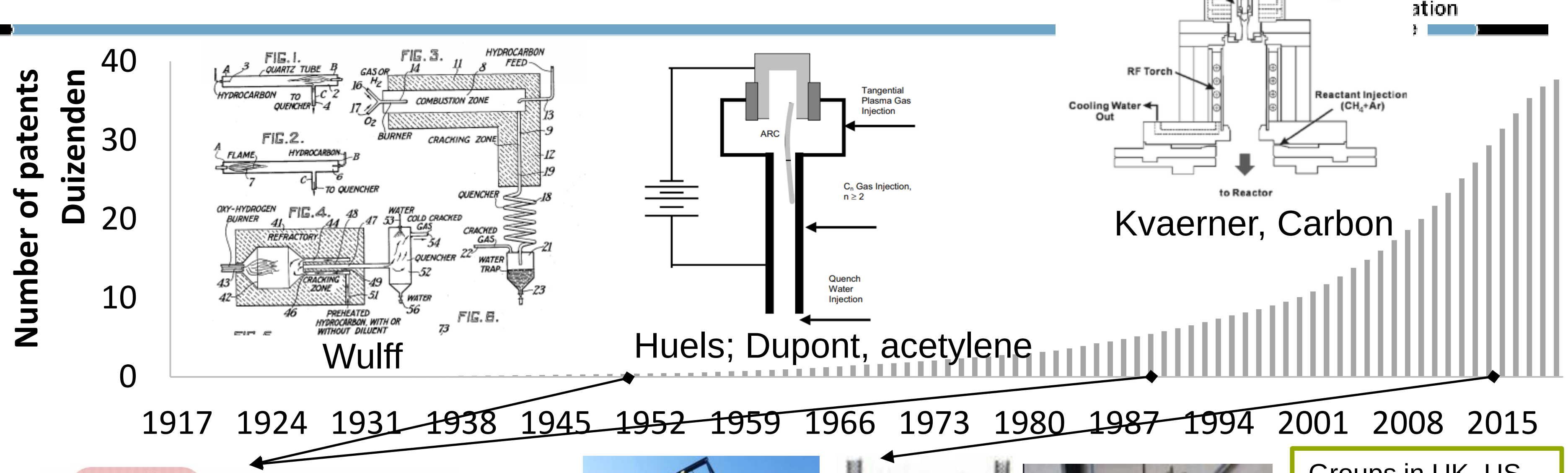
doi.org/10.1016/j.ijhydene.2017.12.081c

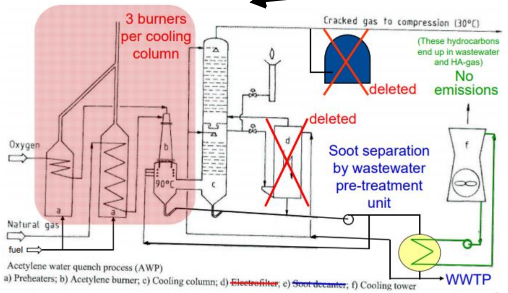
# CONTENTS

# HISTORICAL EVOLUTION FOR METHANE PYROLYSIS



# TIMELINE: METHANE PYROLYSIS




BASF Sachsse, Acetylene

Monolith Materials

BASF

HAZER Group

Groups in UK, US, Spain, Germany, Netherlands are working including companies such as GAZPROM, GASPLAS, ThyssenKrupp, Air Liquide and others.

Formation and separation of carbon has been a major challenge throughout.

# NEW DEVELOPMENTS: CARBON SEPARATION

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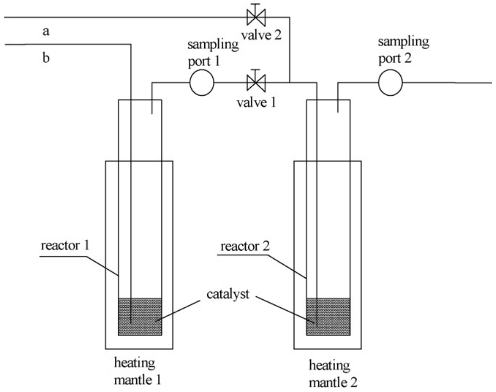
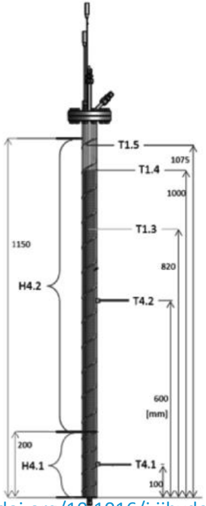
Mg molten metal batch setup




doi:10.1016/j.molcata.2007.12.018

~20% conversion

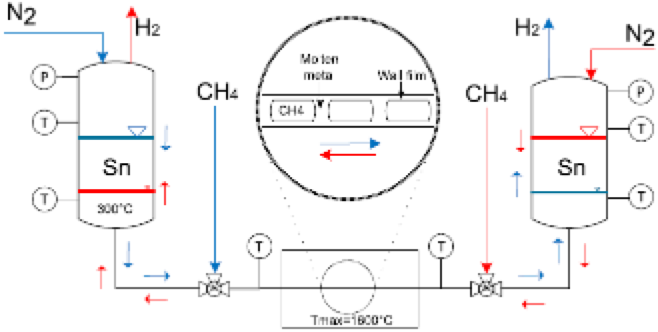
Tin bubble column reactor




http://dx.doi.org/10.1016/j.ijhydene.2015.04.062

~40% conversion

Cappilary slug flow reactor




http://dx.doi.org/10.1016/j.ijhydene.2016.12.044

~80% conversion

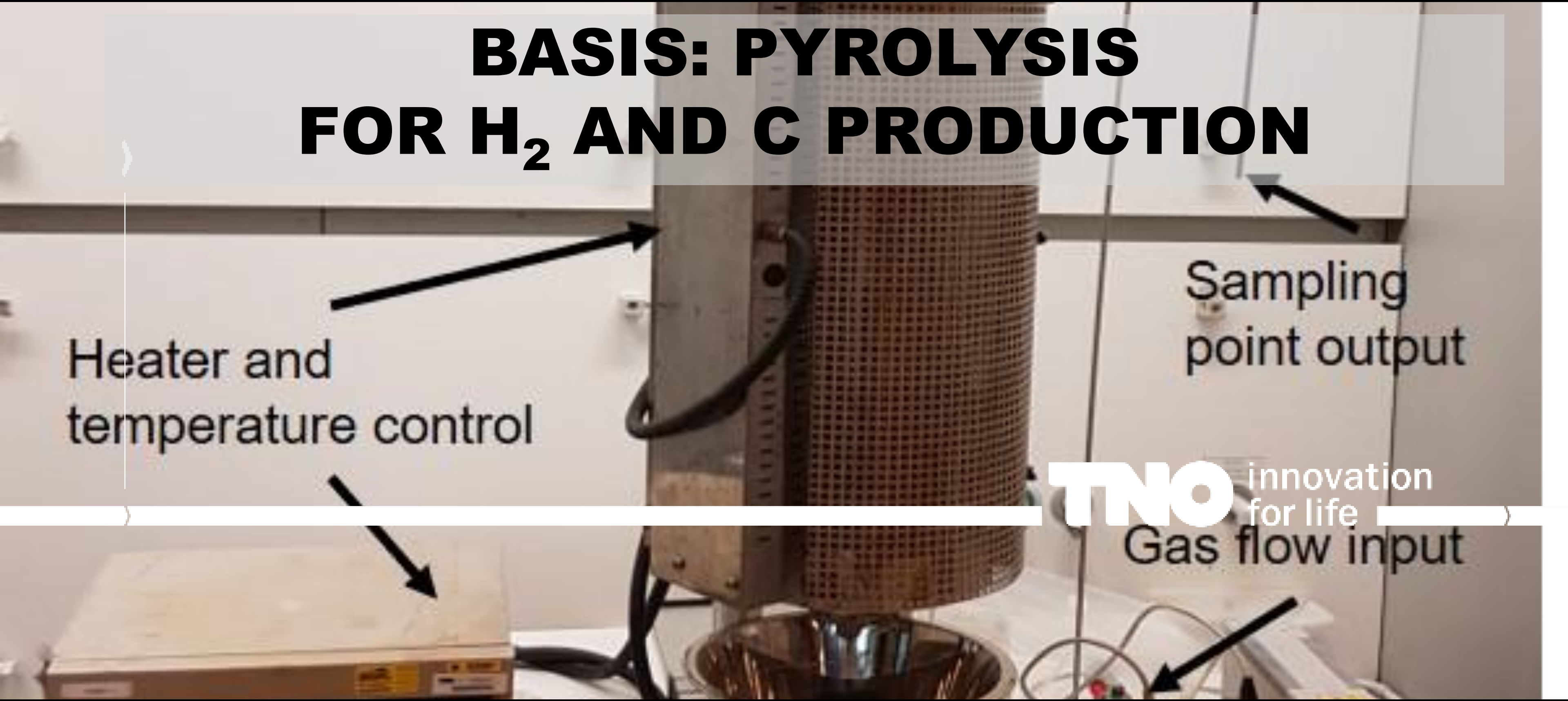
Ni-Bi bubble column reactor

Upham et al., Science 358, 917–921 (2017)

~95% conversion

Advantages of inherently designed separation and floatation of carbon.
Tuning of carbon quality by different conditions and (Ni-Bi) catalyst.

# BASIS: PYROLYSIS FOR $H_2$ AND C PRODUCTION

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# BASIS: PYROLYSIS (MOLTEN METAL) TECHNOLOGY

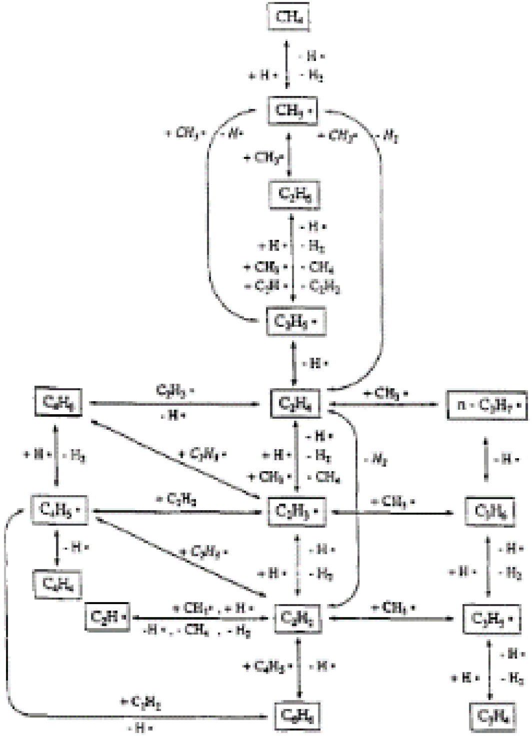
| | | $\Delta H_{Thermodynamic}$ |
|---|---|---|
| Steam methane reforming* | $CH_4 + 2\ H_2O \rightarrow CO_2 + 4H_2$ | 41 kJ/mol $H_2$ |
| $CO_2$ reforming | $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ | 124 kJ/mol $H_2$ |
| Hydrolysis | $H_2O \rightarrow \frac{1}{2} O_2 + H_2$ | 283 KJ/mol $H_2$ |
| Pyrolysis | $CH_4 \rightarrow C + 2H_2$ | 38 KJ/mol $H_2$ |

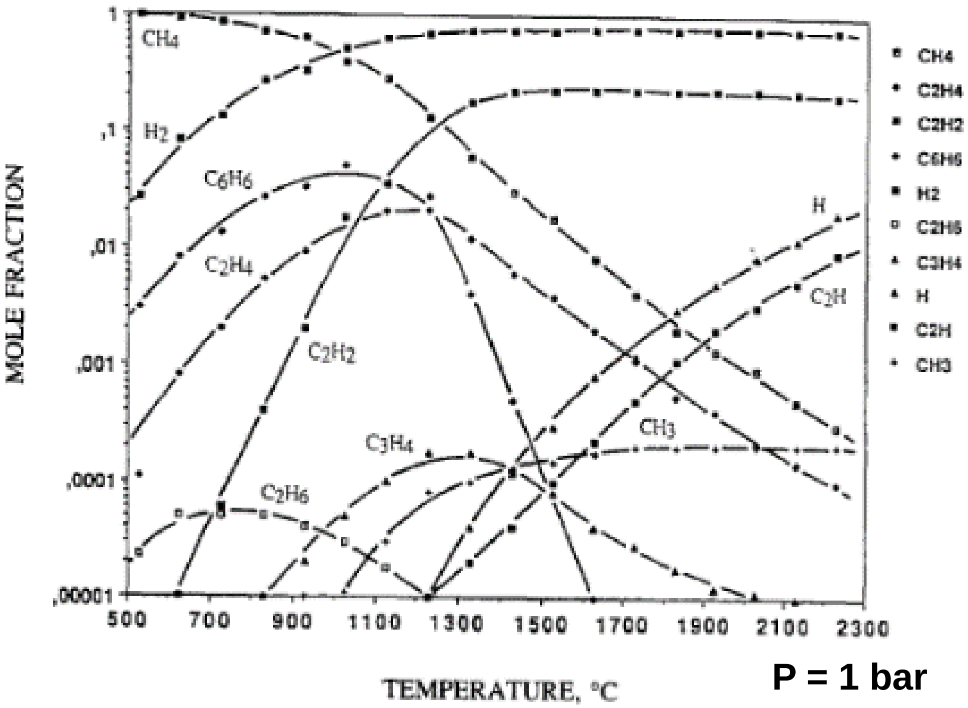
* Water gas shift is included in the reaction equation.

- At 100% conversion, energy/mole reaction is similar for reforming and pyrolysis.
- Steam reforming results in $CO_2$ problem; Pyrolysis results in (solid) carbon product.

# THERMODYNAMICS OF METHANE PYROLYSIS







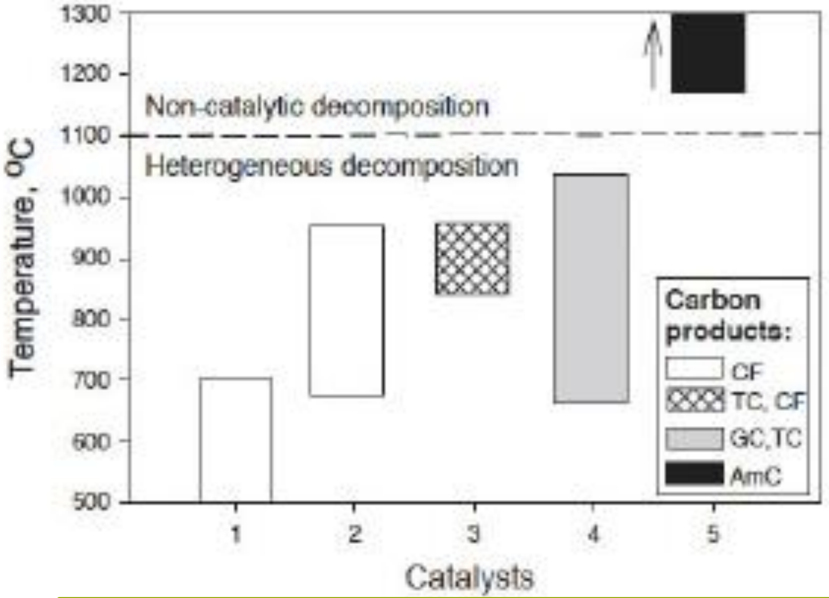

**P = 1 bar**

High temperature is favour carbon formation.
$H_2$ dilution, fast reaction and temperature quench lead to higher carbon atoms products.



doi.org/10.1016/0378-3820(94)00109-7

# IMPACT OF TEMPERATURE CONDITIONS AND CHOICE OF METAL ON CARBON FORMATION




**Decomposition Catalysts:** 1:Ni-based, 2 :Fe-based, 3:carbon-based, 4:Co, Ni, Pd, Pt, Cr, Ru, Mo, and W catalysts, 5:non-catalytic decomposition.

**Carbon products:** CF:carbon filaments, TC:turbostratic carbon, GC:graphitic carbon, AmC:amorphous carbon.

The quality of carbon produced is dependent on the Temperature – catalyst combination.

# EMBER PRINCIPLE

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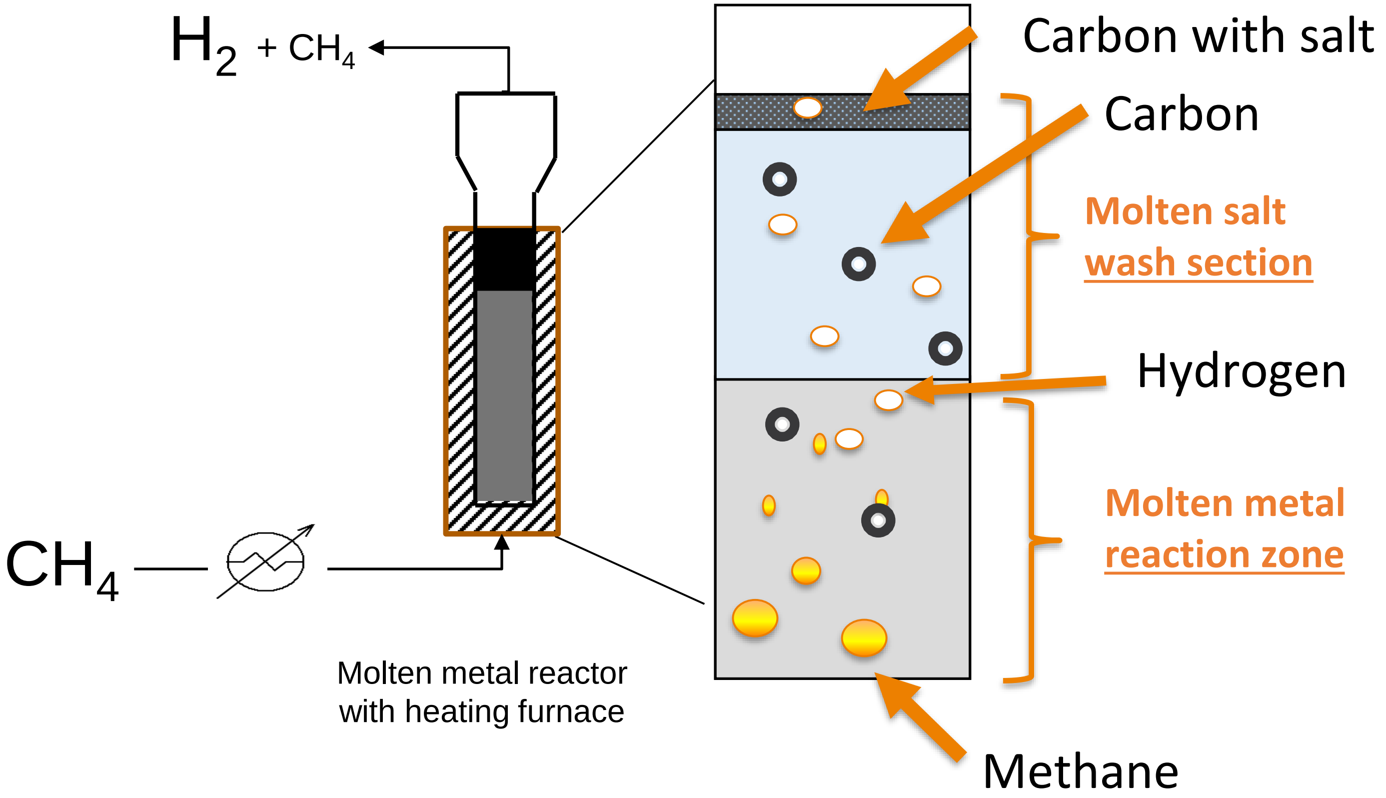
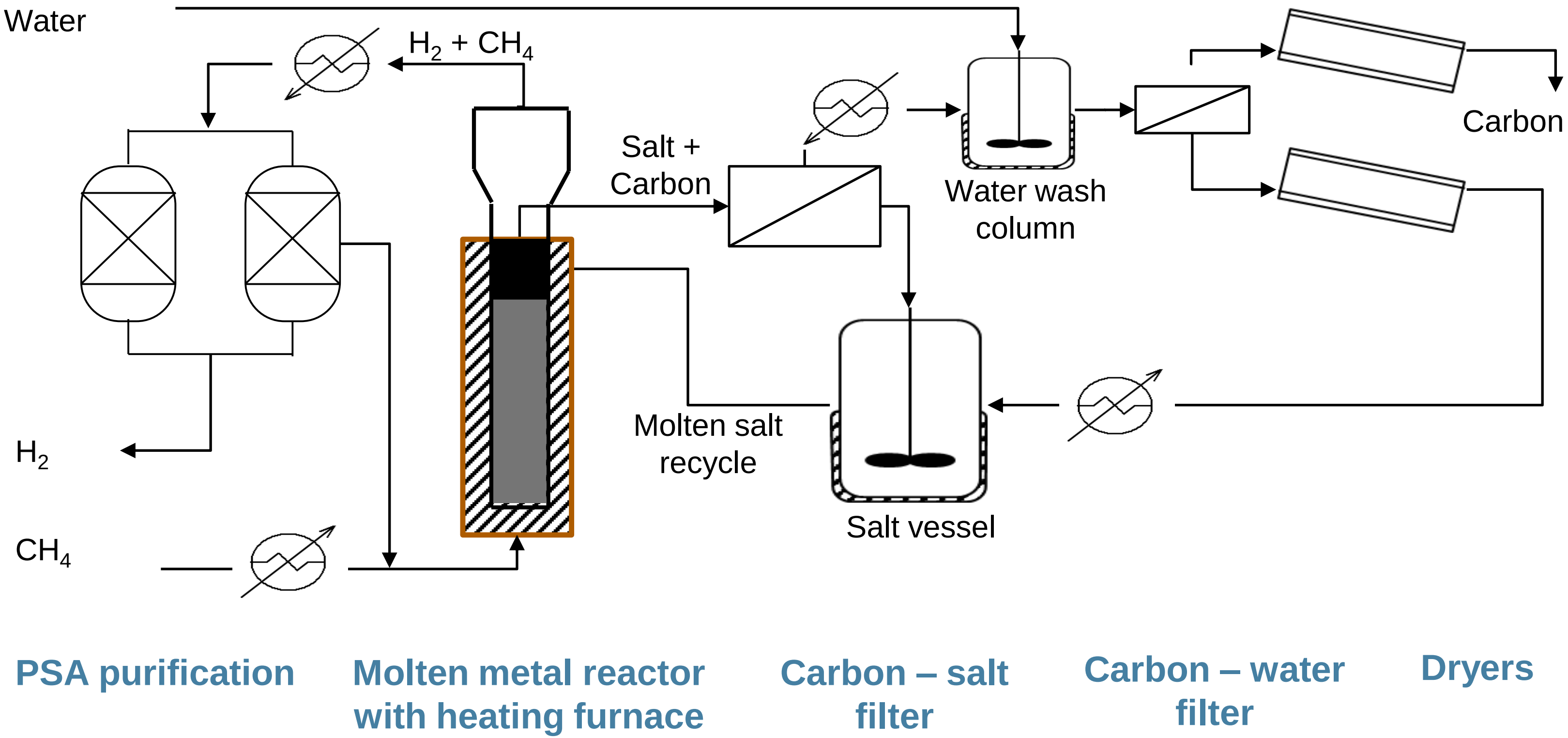


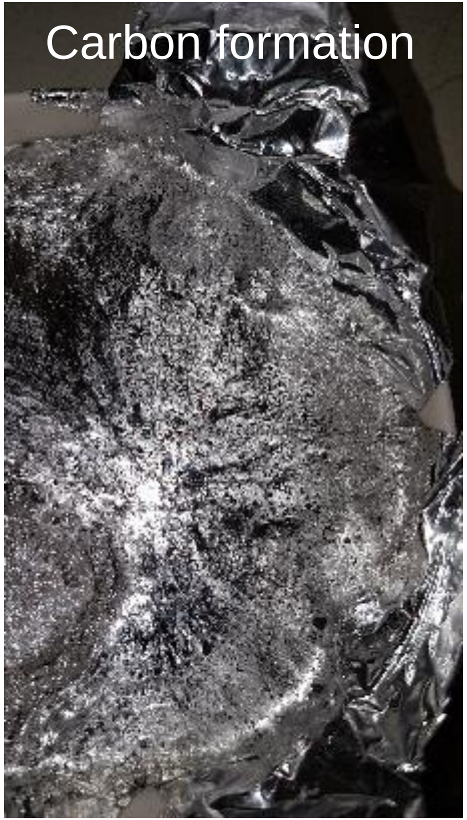
# PROCESS FLOW DIAGRAM WITH CARBON REMOVAL




Pyrolysis reactor and carbon separation in a continuous operation.

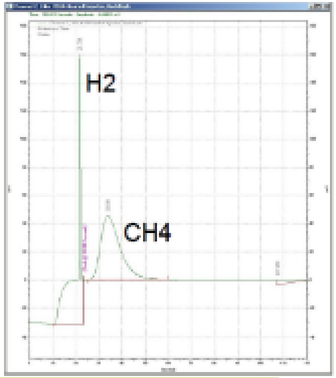
# EXPERIMENTAL VALIDATION

# PROOF OF CONCEPT TESTING (CRACKING)

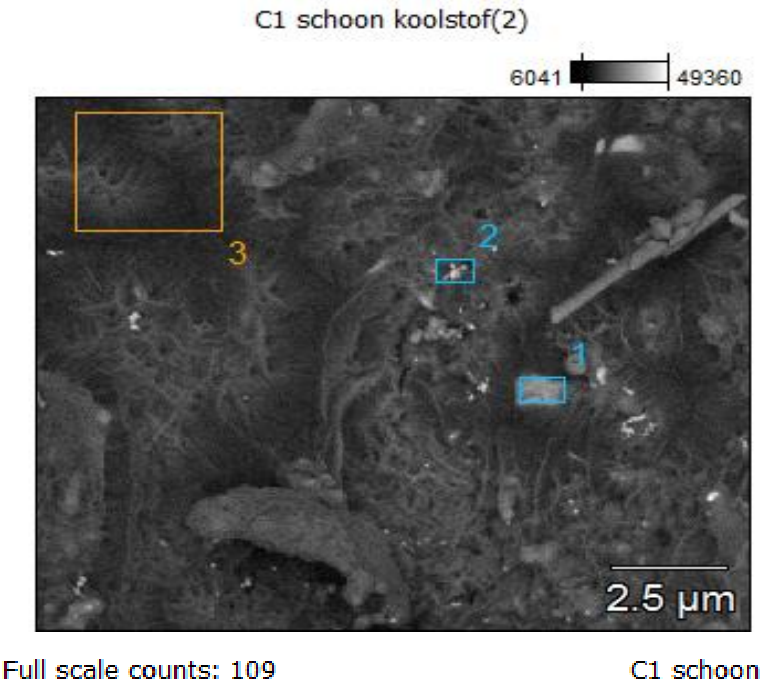


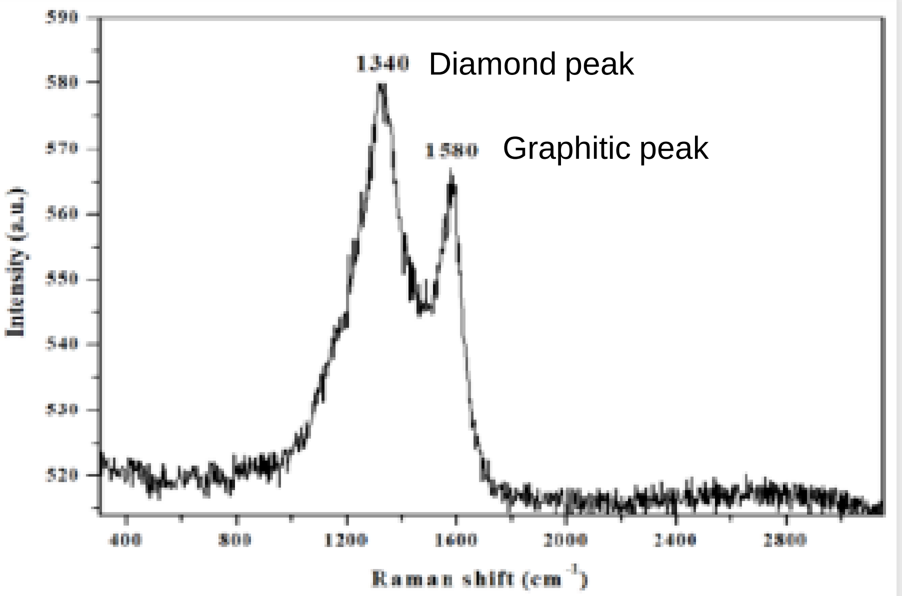
$H_2$
formation




Upto 90% conversion to products from cracking experiments was successfully achieved.

# RESULTS: CARBON ANALYSIS




- Carbon is formed with graphitic characteristics.
- Rod like structures are seen.
- Impurities of gallium (upto 30%) is detected.

# PROOF OF CONCEPT TESTING (SEPARATION OF CARBON)

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| Initial materials | Initial mix | High temperature Separation | Cooling @ room temperature | Separation |
| --- | --- | --- | --- | --- |

## Initial materials

Gallium

+

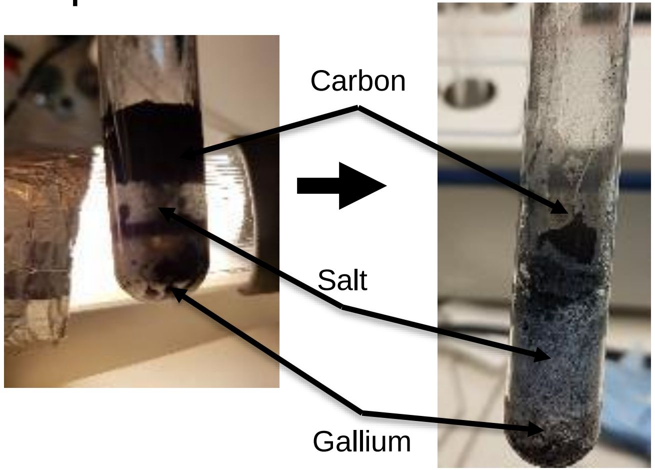
Salt

+

Carbon
Particle size: < 100 µm.

## Initial mix

## High temperature Separation / Cooling @ room temperature




Re-arrangement of carbon, salt and molten metal. Carbon separated on top due to its low density.

Salt solidifies, metal remains liquid around room temperature and carbon is separated at top.

## Separation



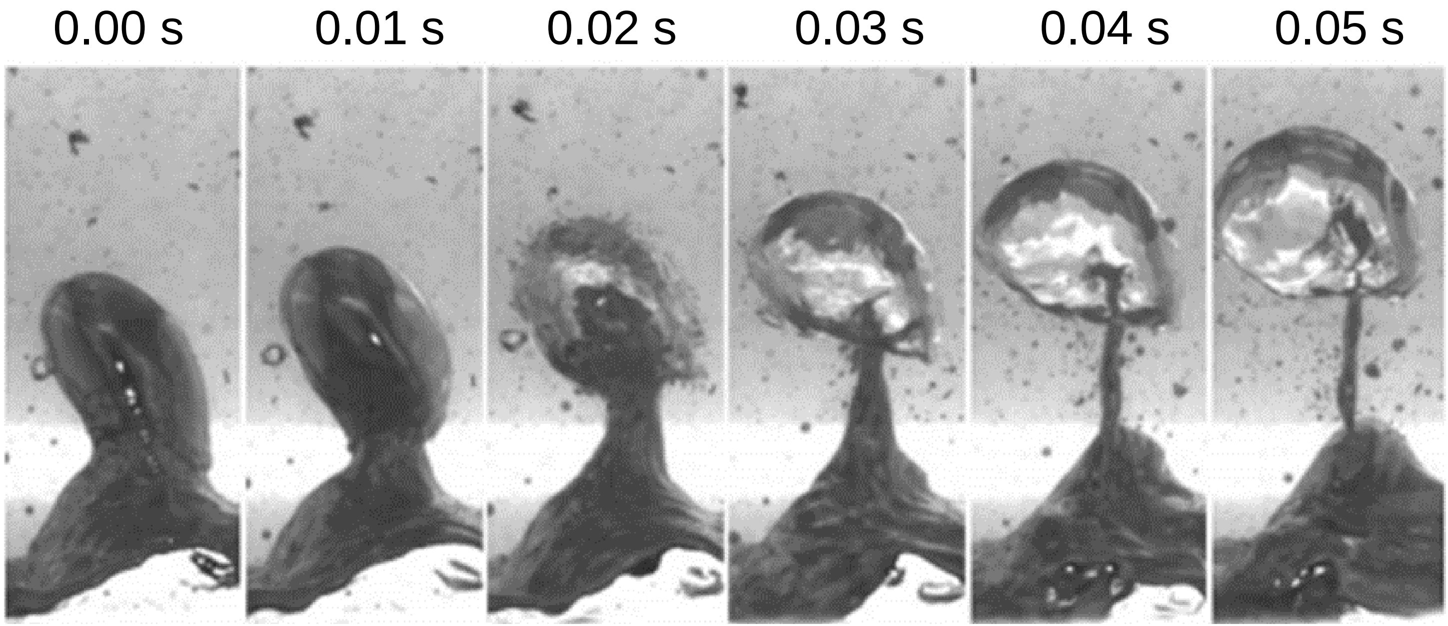

> 96% carbon was recovered in the salt layer with continuous bubbling of gas.

# SALT SELECTION

- Key parameters:
  - Density : Intermediate density between carbon and molten metal;
  - Salt adhesion to carbon: Low to prevent wetting of carbon by salt.
  - Cost and safety: To limit the overall cost of production and handling.
  - Residence time of salt wash: Long enough to be able to wash metal layer from the carbon.
  - Melting point and vapor pressure: Low vapor pressure at reaction temperature.

Out of an initial list of 35 salts, seven salts were experimentally tested.

# SALT SELECTION - WETTABILITY




Adhesion of graphite on salt ~ (Cation radius)$^2$/ Anion radius

NaBr, NaCl are more preferable than CsCl and KBr



Adapted from doi.org/10.1016/j.msea.2007.11.093

# SALT SELECTION – DENSITY

Separation by flotation

Low density salt

High Density salt

- Separation due to flotation and density differences successfully achieved.
- NaCl, NaBr $ZnCl_2$ able to separate by flotation; NiCl, CuCl, $MgCl_2$ by density.

# DOWNSTREAM PROCESSING: FILTRATION

Initial state | Final state

Pore size – 4 – 8 µm

Initial state | Final state

Pore size – 25 – 50 µm

- Both filters are able to separate salt from carbon – salt homogeneous mix.
- Filter with poresize of  25 - 50 micrometer has higher rate of filteration than 4 – 8 micrometer filter.

# DOWNSTREAM PROCESSING – FILTRATION AND CLEANING

| | Initial | After filtration and water wash | After acid wash |
|---|---|---|---|
| Metal % | 31.1 | 0.7 | 0.0 |
| Carbon% | 68.9 | 95.1 | 97.3 |
| Salt % | 0.0 | 4.2 | 2.7 |

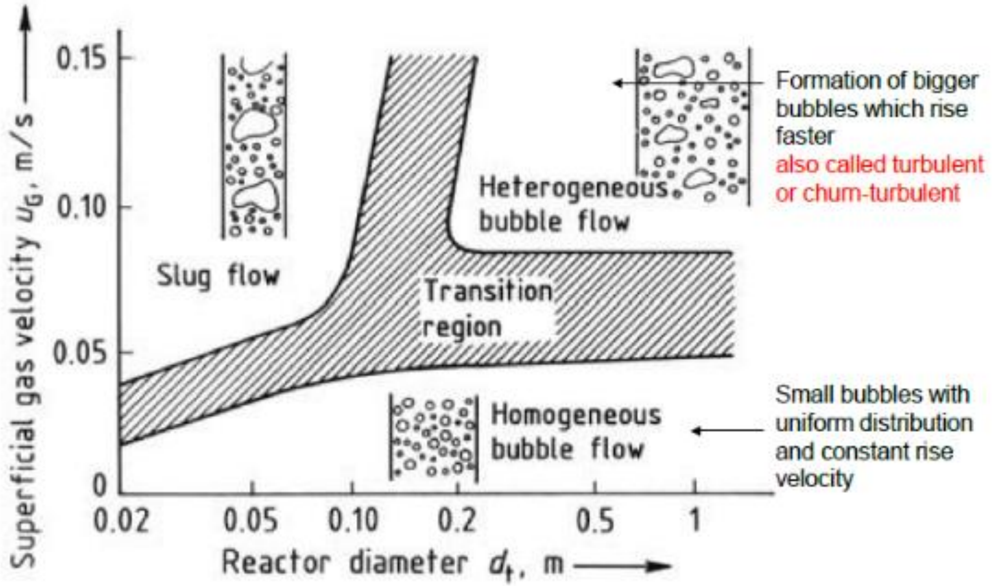
Metal chlorides/ bromides have shown successful separation and cleaning of carbon.

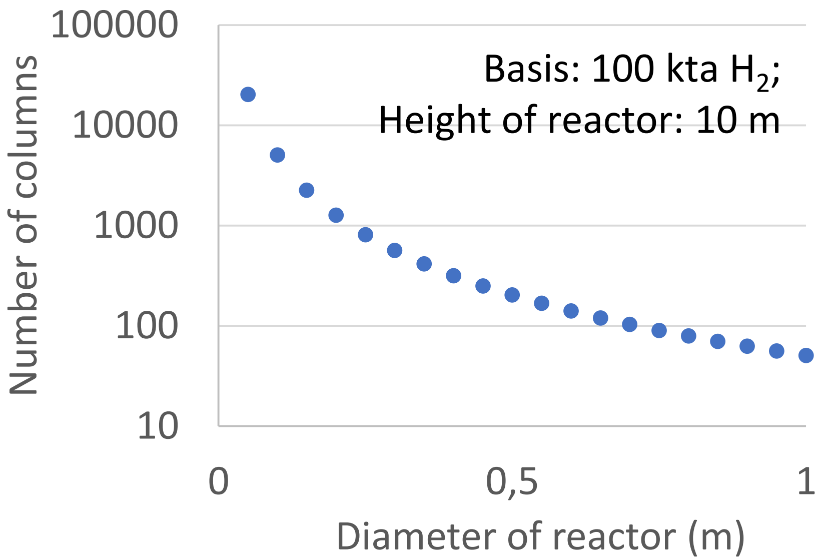


Adapted from doi.org/10.1016/j.carbon.2019.05.041

# SCALE UP, OPTIMIZATION AND REACTOR DESIGN

# BUBBLE SIZE AND HYDRODYNAMICS




- Normal bubble sizes (~1-5 mm) limit scaling up of reactor.
- 100 Kta $H_2$ production would mean at least 100 columns of diameter of 0.75 m and 10 m in height ~ 600 $m^3$.

# INTENSIFIED REACTOR DESIGN: MICROBUBBLE INJECTION

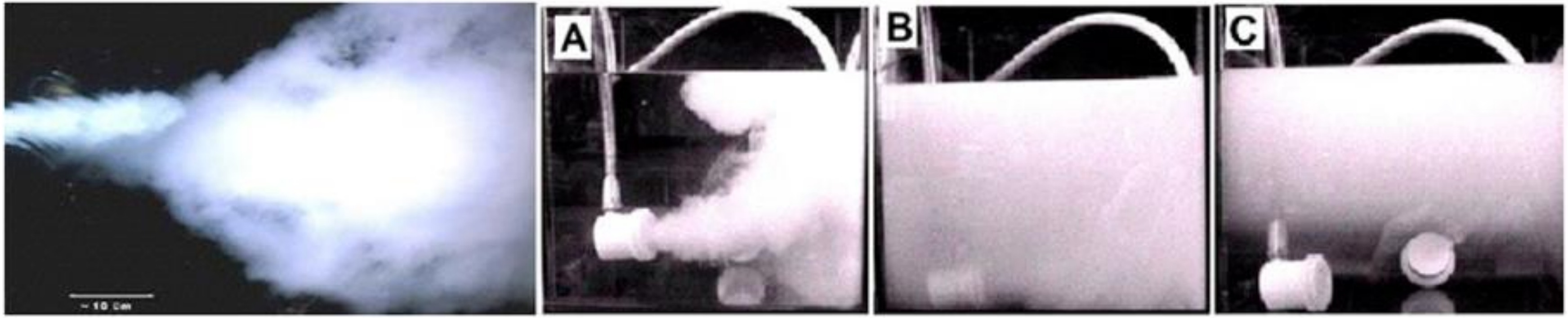



**Figure 1.** Microbubble sparging [Seitz 2010]. Sparging is stopped at image B and image C is 120 s later. Manufacturer claim for bubble size is ~1 µm, though the implied rise velocity is consistent with a radius of ~20 µm, perhaps with smaller bubbles having dissolved.

- 100 X increase in surface area.
- 5 X decrease in rise velocity.
- 500 X decrease in reactor volume.

# TECHNO-ECONOMICS AND BUSINESS CASES

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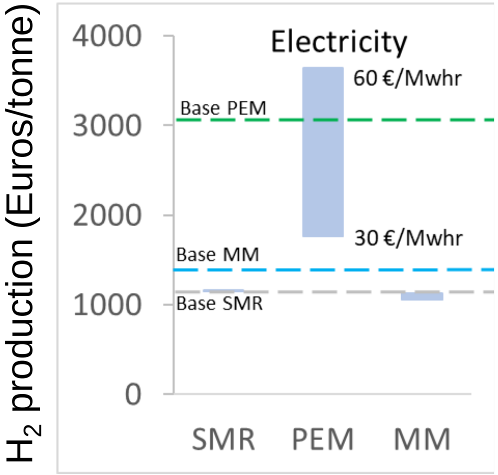
# WHAT ABOUT ECONOMICS?

## Marginal cost estimates (excluding CAPEX and profits)




Base case values:

| | | | | |
|---|---|---|---|---|
| Electricity | 50 | EUR/MWh | Carbon | 100EUR/t |
| Gas/ Heat | 6 | EUR/GJ | Steam | 21EUR/t |
| CO2 tax | 25.96 | EUR/t | Carbon credit | 25.96EUR/t |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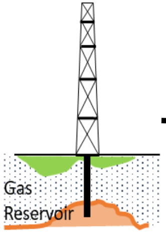
**Pyrolysis of methane is most attractive when carbon has a value in combination with a $CO_2$ tax.**

# WHY DO LARGE SCALE PYROLYSIS?

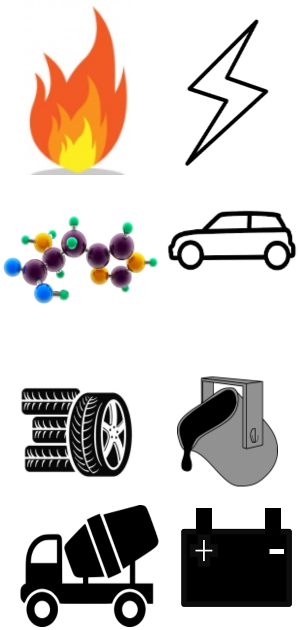



Bio gas production

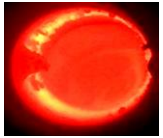
$C_xH_y$

$H_2$

C



| Conventional | EMBER |
| --- | --- |
| 9 – 11 tonnes $CO_2$/ton $H_2$ | 0-2.5 TONNES CO2/ TON H2 + 3 TON C |
| 2.5 – 4.5 tonnes $CO_2$/ton C | |



ABUNDANT RAW MATERIALS

$H_2$ & C ARE BASE PRODUCTS

**EMBER: a cost effective process for producing hydrogen and carbon**

# Ember

## PYROLYSIS TECHNOLOGY FOR HYDROGEN AND CARBON

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Take a look:

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**Rajat Bhardwaj, Willem Frens, Marco Linders, Earl Goetheer**

# THANK YOU FOR YOUR ATTENTION


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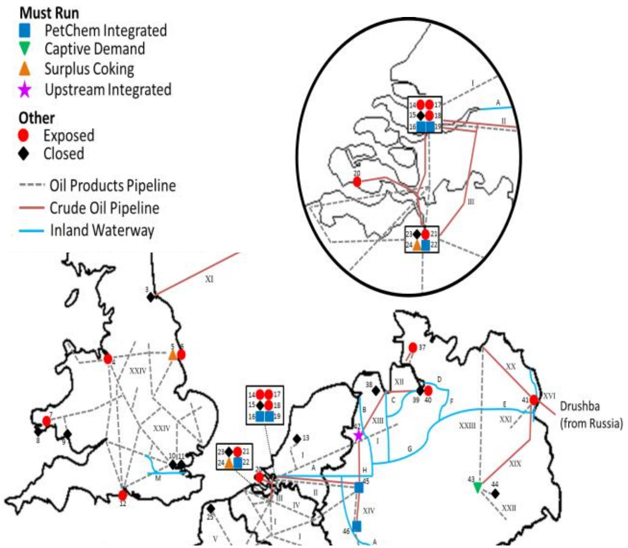
# APPENDIX

Renewable revolution




Focus Driven

Value Generator

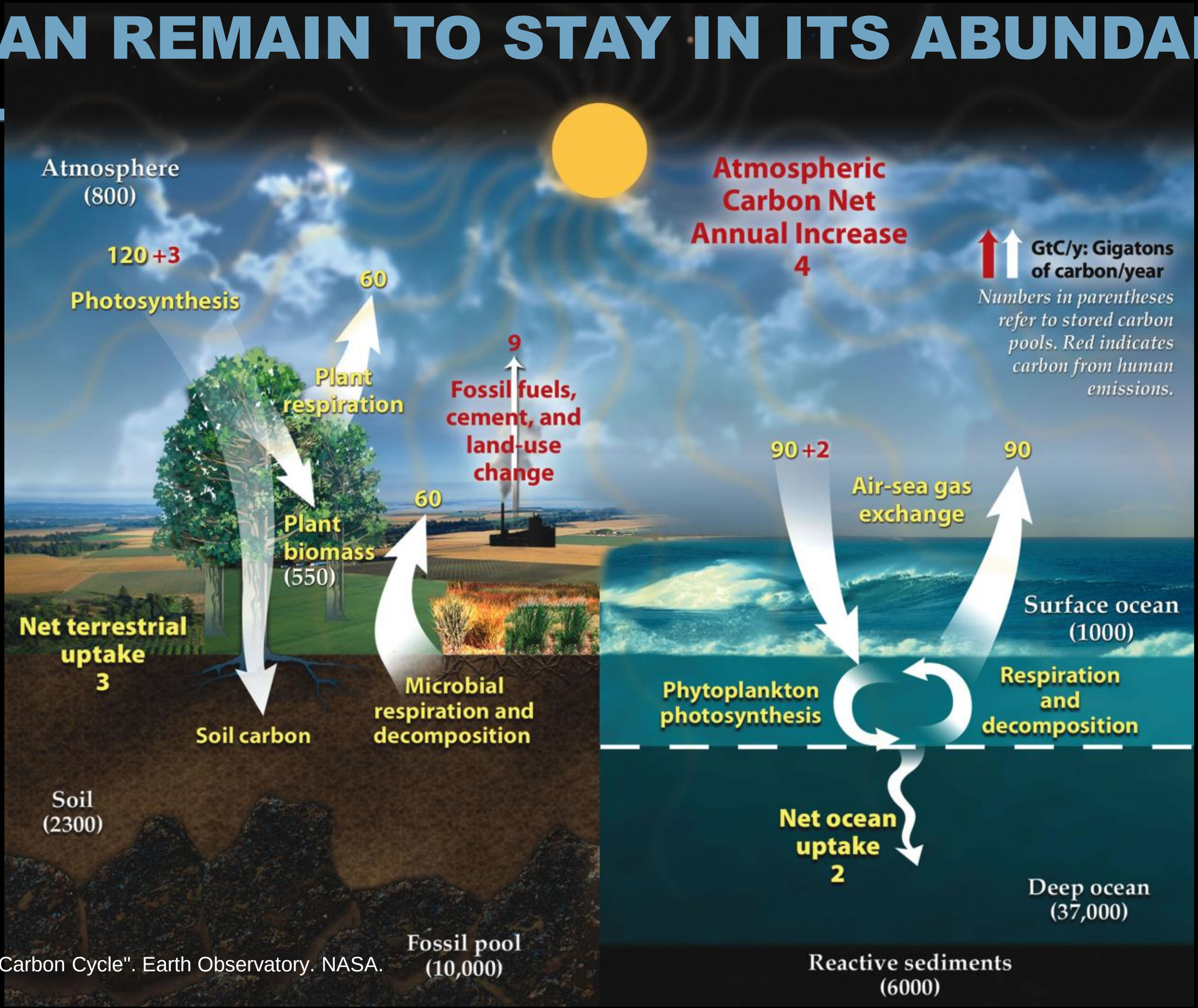
Climate Frontrunner

In Rotterdam:

- Companies with global outreach.
- Connection with skilled human resource.
- Enough fuel gas to decarbonize >35% emissions.
- Framework for moving towards change.

North-west Europe holds potential to be the frontrunner in low carbon technology demonstration.

# CARBON CAN REMAIN TO STAY IN ITS ABUNDANT FORM




Riebeek, Holli (16 June 2011). "The Carbon Cycle". Earth Observatory. NASA.

# WHAT ABOUT ECONOMICS AND LIFE CYCLE?

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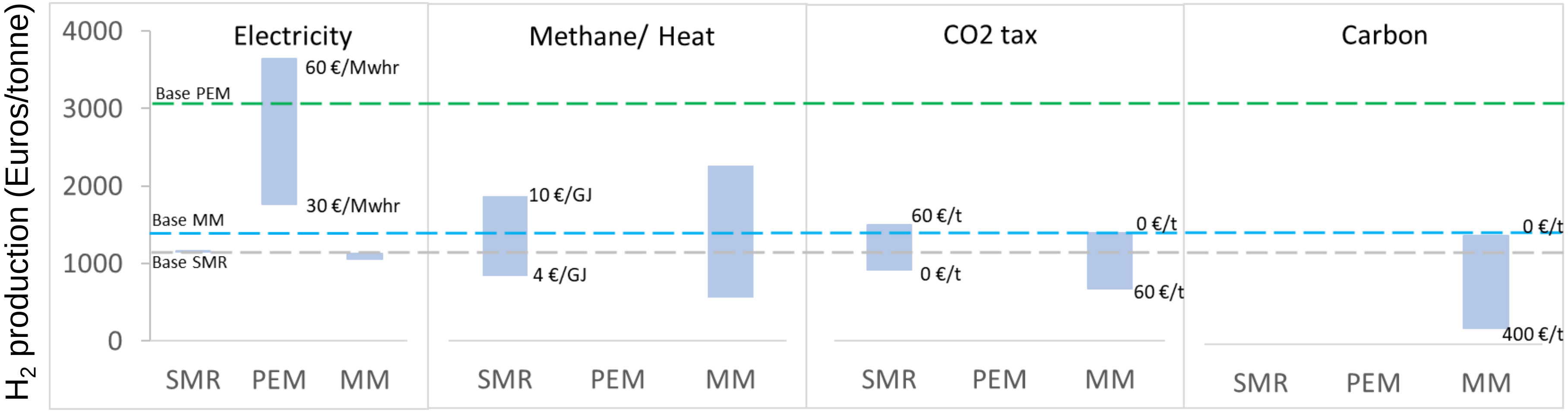
Marginal cost estimates (excluding CAPEX) for $H_2$ production




Pyrolysis of methane is most attractive when carbon has a value in combination with a $CO_2$ tax.

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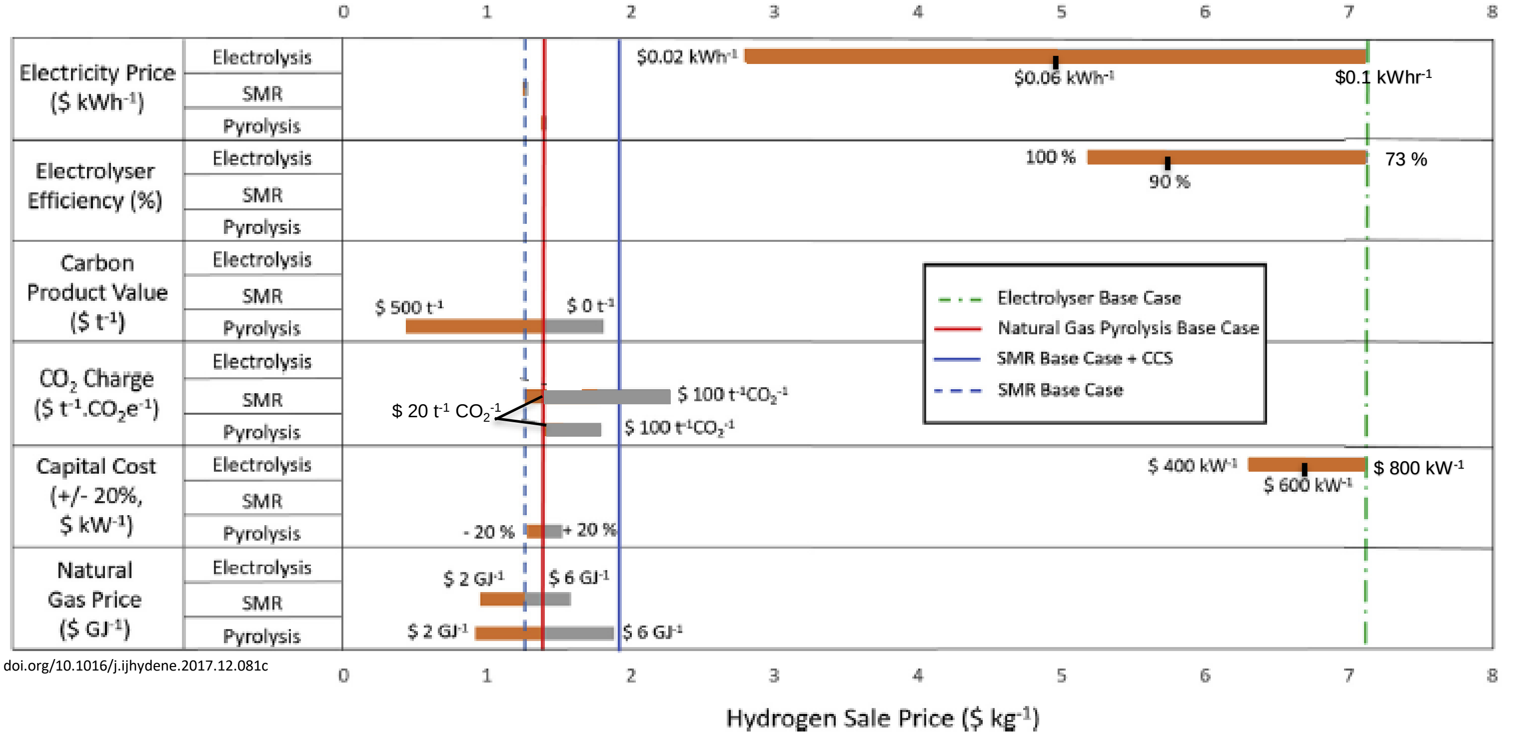



doi.org/10.1016/j.ijhydene.2017.12.081c

Economics sensitive towards

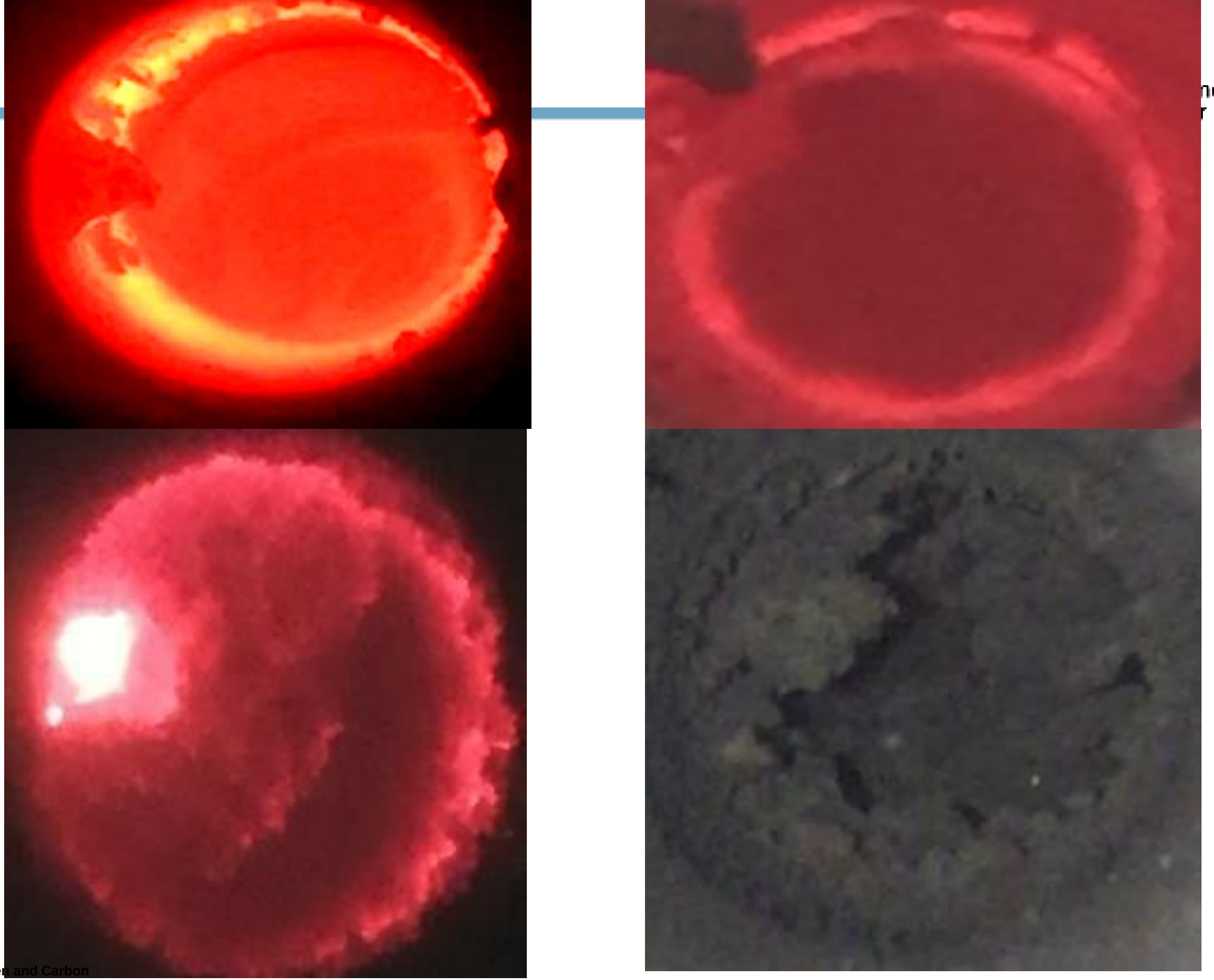
- value of carbon and
- $CO_2$ penalty.

Base costs for analysis:

| | |
|---|---|
| Natural gas price | 4 $/GJ |
| Electricity price (grid) | 60 $/MWhr |
| Electricity price (green) | 100 $/MWhr |
| Steam (30 bars) | 30 $/tonne |

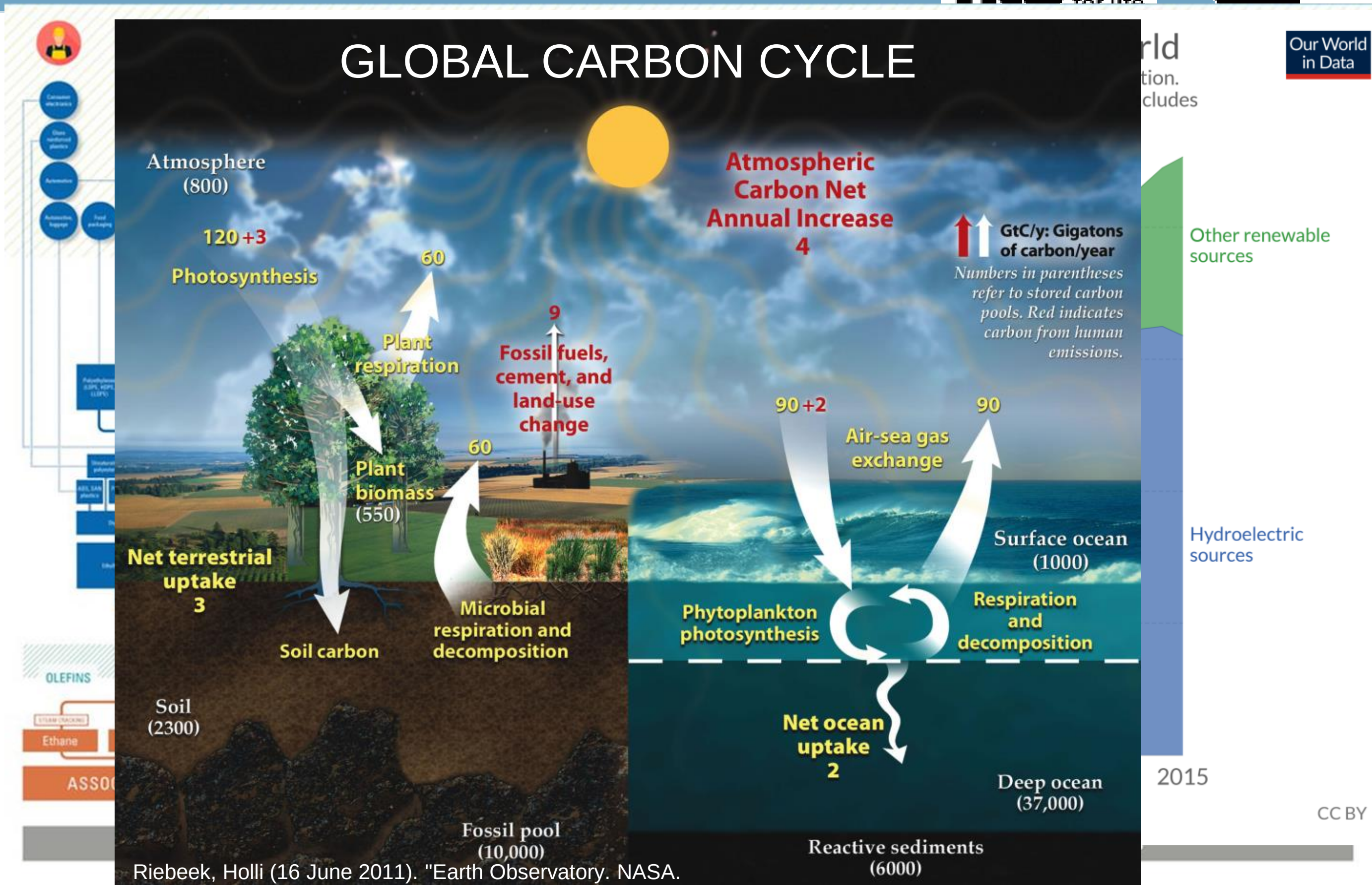


doi.org/10.1016/j.ijhydene.2017.12.081



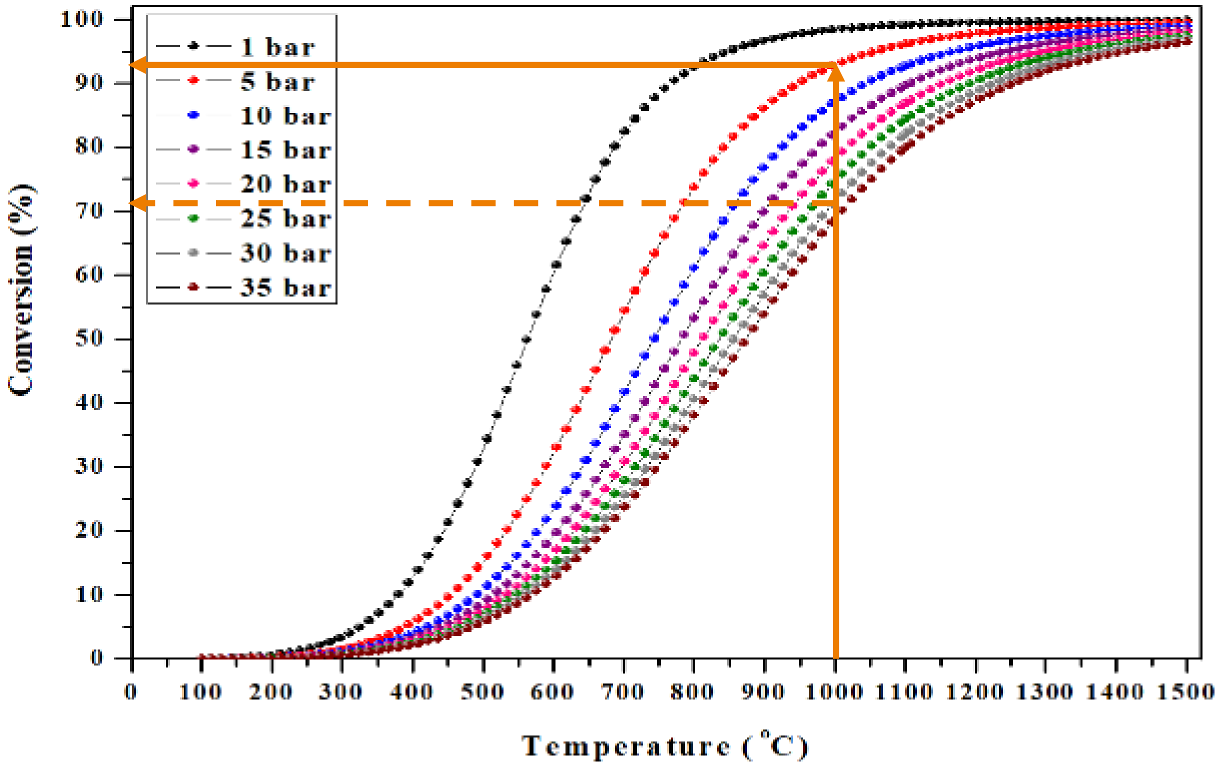
# WHY DO LARGE SCALE (MOLTEN METAL) PYROLYSIS?

- Abundantly resource to two valuable products $H_2$ and solid carbon.
- $H_2$ and carbon are backbone for human survival.
- The traditional routes are highly emitting
- $CO_2$ problem to carbon opportunity.



Riebeek, Holli (16 June 2011). "Earth Observatory. NASA.

# REACTOR OPERATING CONDITIONS




Design temperature of 1000 $^0$C and P ~ 5bars can result a conversion of > 90%.

Thermal decomposition of methane via molten metal, B Perez, (2019)

# POTENTIAL MAPPING OF CARBON + $H_2$ MARKET

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| Type of Carbon | Types of Applications | Expected Price for Carbon | Size of the Market (current/ projected) | Corresponding Hydrogen Production[(a)] |
|---|---|---|---|---|
| Carbon black [1] [2] [3] | Tires, printing inks, high-performance coatings and plastics | $0.4–2+ /kg depending on product requirements | U.S. market<br>• ~ 2M MT (2017)<br><br>Global market<br>• 12M MT (2014)<br>• 16.4M MT (2022) | U.S. market<br>• 0.67M MT<br><br>Global market<br>• 4M MT (2014)<br>• 5.4M MT (2022) |
| Graphite [4] | Lithium-ion batteries | $10+/kg | Global market<br>• 80K MT (2015)<br>• 250K MT (2020) | Global market<br>• 27K MT (2015)<br>• 83K MT (2020) |
| Carbon fiber [5] [6] [7] | Aerospace, automobiles, sports and leisure, construction, wind turbines, carbon-reinforced composite materials, and textiles | $25–113/kg depending on product requirements | Global market<br>• 70K MT (2016)<br>• 100K MT (2020) | Global market<br>• 23.3K MT (2016)<br>• 33.3K MT (2020) |
| Carbon nanotubes [8] [9] | Polymers, plastics, electronics, lithium-ion batteries | $0.10–600.00 per gram depending on application requirements | Global market<br>• 5K MT (2014)<br>• 20K MT (2022) | Global market<br>• 1.7K MT (2014)<br>• 6.7K MT (2022) |
| Needle coke [10] | Graphite electrodes for electric arc steel furnaces | ~$1.5/kg | Global market<br>• ~1.5M MT (2014) | Global market<br>• ~0.50M MT (2014) |

(a) Based on stoichiometric ratio of carbon to hydrogen present in methane. Does not take into account process efficiency or use of hydrogen to provide process heat or loss of hydrogen during hydrogen recovery.

R&D Opportunities for Development of Natural Gas Conversion Technologies, Argonne (2017)

The carbon and $H_2$ market is of significant size to be produced and used at large scale.
New markets need to be developed for continued deployment of high value use for carbon.

# CATALYTICAL ACTIVITY OF MOLTEN METALS

**Table 1. Comparison of activity for methane pyrolysis at 1000°C when $CH_4$ is flowed over 38.5 mm$^2$ of molten metal as described in fig. S1a.** The same reactor volume was used in all cases, including for Pb vapor. All compositions are molar percent. An asterisk (*) indicates that alloy is at the solubility limit of the dissolved active metal at 950°C.

| Liquid catalyst | Rate of hydrogen production (mol $H_2$ produced × cm$^{-2}$ s$^{-1}$) |
|---|---|
| In | $8.2 \times 10^{-11}$ |
| Bi | $8.2 \times 10^{-11}$ |
| Sn | $8.5 \times 10^{-10}$ |
| Ga | $3.2 \times 10^{-9}$ |
| Pb | $3.3 \times 10^{-9}$ |
| Ag | $4.3 \times 10^{-9}$ |
| Pb vapor | $2.1 \times 10^{-9}$ |
| 17% Cu-Sn* | $3.1 \times 10^{-9}$ |
| 17% Pt-Sn | $1.6 \times 10^{-9}$ |
| 17% Pt-Bi | $4.2 \times 10^{-9}$ |
| 62% Pt-Bi* | $6.5 \times 10^{-9}$ |
| 17% Ni-In | $4.7 \times 10^{-9}$ |
| 17% Ni-Sn | $5.6 \times 10^{-9}$ |
| 73% Ni-In* | $6.4 \times 10^{-9}$ |
| 17% Ni-Ga | $7.9 \times 10^{-9}$ |
| 17% Ni-Pb | $8.3 \times 10^{-9}$ |
| 17% Ni-Bi | $9.0 \times 10^{-8}$ |
| 27% Ni-Au* | $1.2 \times 10^{-8}$ |
| 27% Ni-Bi* | $1.7 \times 10^{-8}$ |
| 27% Ni-Bi* (replicate)* | $1.7 \times 10^{-8}$ |

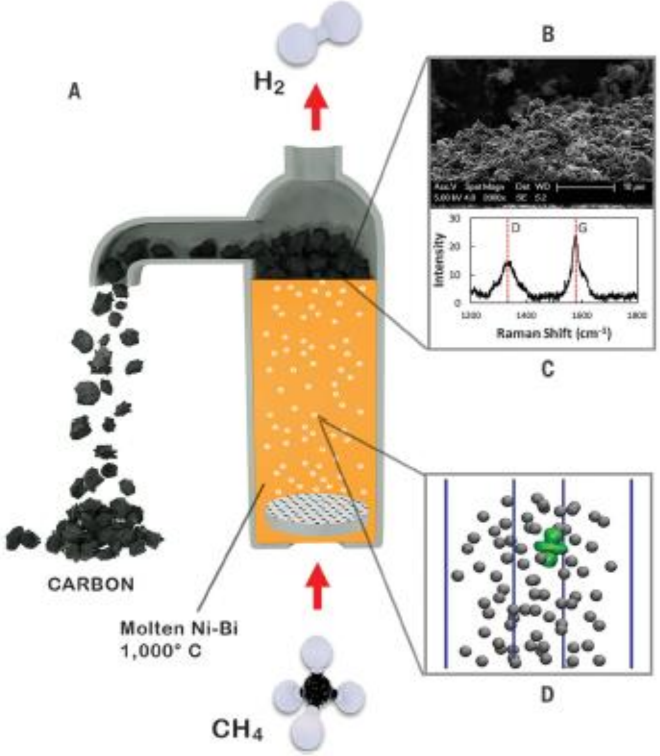


**Fig. 1. Hydrogen production with a Ni-Bi molten catalyst.** (**A**) Reactor for $CH_4$ conversion to $H_2$ and carbon in a molten-metal bubble column with continuous carbon removal. (**B**) Scanning electron microscopy image of the carbon produced. (**C**) Raman spectrum of surface carbon. The dashed line labeled "D" is at 1350 cm$^{-1}$, and the dashed line labeled "G" is at 1582 cm$^{-1}$. (**D**) Ab initio molecular dynamics simulation showing an orbital (green) of a Pt atom dissolved in molten Bi (gray) alloy.



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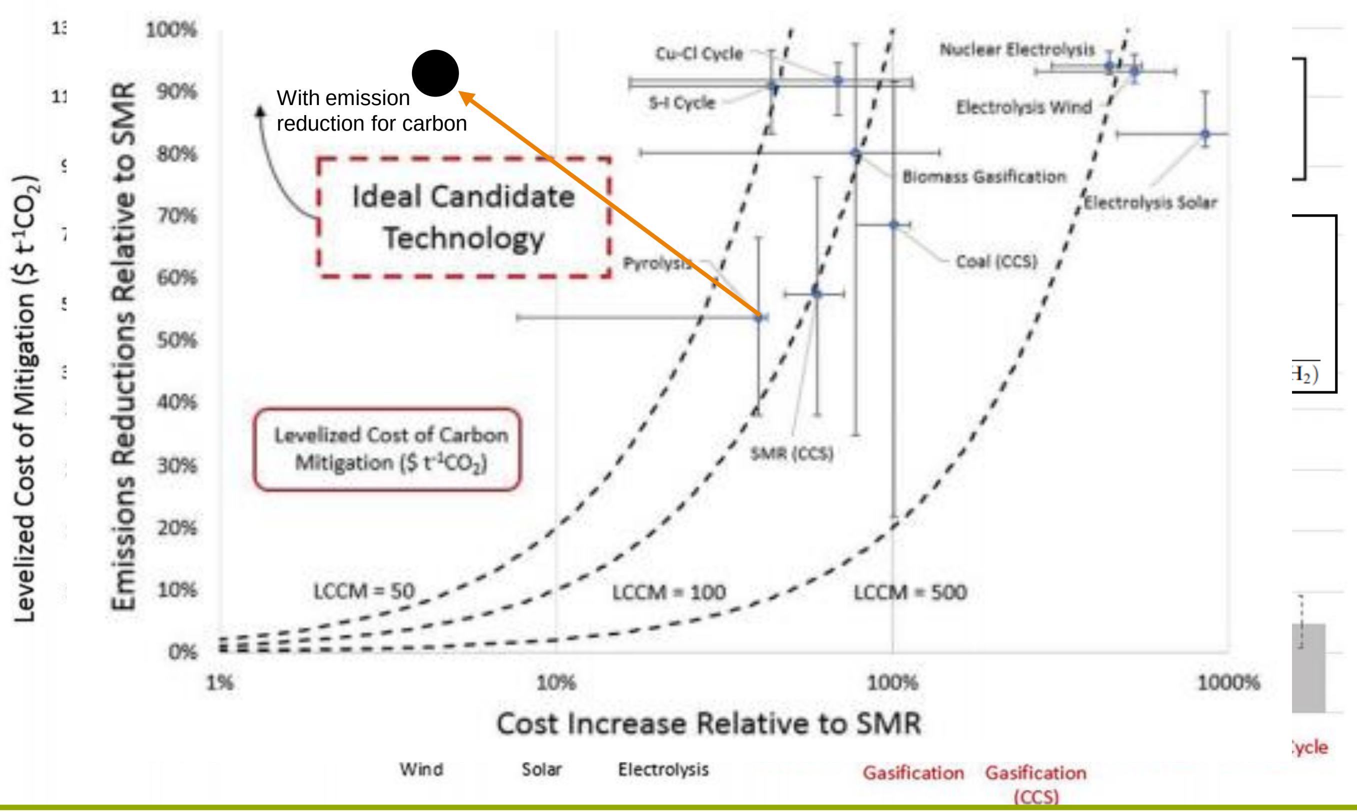
# BASIS: PYROLYSIS (MOLTEN METAL) TECHNOLOGY

| | | $\Delta H_{Thermodynamic}$ | |
|---|---|---|---|
| Steam methane reforming* | $CH_4 + 2\ H_2O \rightarrow CO_2 + 4H_2$ | 165 kJ/mol | 41 kJ/mol $H_2$ |
| $CO_2$ reforming | $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ | 247 kJ/mol | 124 kJ/mol $H_2$ |
| Hydrolysis | $H_2O \rightarrow ½\ O_2 + H_2$ | 283 kJ/mol | 283 KJ/mol $H_2$ |
| Pyrolysis | $CH_4 \rightarrow C + 2H_2$ | 76 kJ/mol | 38 KJ/mol $H_2$ |

* Water gas shift is included in the reaction equation.

- At 100% conversion, energy/mole reaction is similar for reforming and pyrolysis.
- Steam reforming results in $CO_2$ problem; Pyrolysis results in (solid) carbon product.

# WHAT ABOUT ECONOMICS AND LIFE CYCLE?




Fossil based H2 production are required for low cost for decarbonization but may not be enough towards ambitious climate goals.

Note: Biomass with CCS, emissions reduction of 213% and a cost increase of 168%, has been omitted from the chart as an outlier to allow focus on other technologies.
$CO_2$ Mitigation for carbon production not considered.

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